Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

CrossMark

Assessment of primary and secondary ambient particle trends using satellite aerosol optical depth and ground speciation data in the New England region, United States

Hyung Joo Lee [a,*], Choong-Min Kang [a], Brent A. Coull [b], Michelle L. Bell [c], Petros Koutrakis [a]

[a] Exposure, Epidemiology, and Risk Program, Department of Environmental Health, Harvard School of Public Health, Boston, MA, USA
[b] Department of Biostatistics, Harvard School of Public Health, Boston, MA, USA
[c] School of Forestry and Environmental Studies, Yale University, New Haven, CT, USA

ARTICLE INFO

ABSTRACT

The effectiveness of air pollution emission control policies can be evaluated by examining ambient pollutant concentration trends that are observed at a large number of ground monitoring sites over time. In this paper, we used ground monitoring measurements in conjunction with satellite aerosol optical depth (AOD) data to investigate fine particulate matter ($PM_{2.5}$; particulate matter with aerodynamic diameter ≤ 2.5 μm) trends and their spatial patterns over a large U.S. region, New England, during 2000–2008. We examined the trends in rural and urban areas to get a better insight about the trends of regional and local source emissions. Decreases in $PM_{2.5}$ concentrations (μg/m^3) were more pronounced in urban areas than in rural ones. In addition, the highest and lowest $PM_{2.5}$ decreases (μg/m^3) were observed for winter and summer, respectively. Together, these findings suggest that primary particle concentrations decreased more relative to secondary ones. This is also supported by the analysis of the speciation data which showed that downward trends of primary pollutants including black carbon were stronger than those of secondary pollutants including sulfate. Furthermore, this study found that ambient primary pollutants decreased at the same rate as their respective source emissions. This was not the case for secondary pollutants which decreased at a slower rate than that of their precursor emissions. This indicates that concentrations of secondary pollutants depend not only on the primary emissions but also on the availability of atmospheric oxidants which might not change during the study period. This novel approach of investigating spatially varying concentration trends, in combination with ground $PM_{2.5}$ species trends, can be of substantial regulatory importance.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Fine particulate matter ($PM_{2.5}$; particulate matter with aerodynamic diameter ≤ 2.5 μm) is a mixture of local and regional pollutants including sulfate, nitrate, ammonium, organic and elemental carbon, metal oxides, and crustal compounds (U.S. EPA, 2004). The particles originating from anthropogenic and natural sources are released directly from the sources (i.e., primary pollution) or are formed in the atmosphere largely through photochemical reaction from precursor gases (i.e., secondary pollution). Numerous studies have demonstrated that ambient $PM_{2.5}$ concentrations are associated with adverse human health and environmental effects (Bell et al., 2007, 2010; Dockery et al., 1993; Gent et al., 2003, 2009; Ramanathan et al., 2001). The World Health Organization (WHO) annual and 24-h $PM_{2.5}$ guidelines are 10 and 25 μg/m^3, respectively (WHO, 2005). In the U.S. Environmental Protection Agency (EPA) (U.S. EPA, 2012) $PM_{2.5}$ standards are 12 μg/m^3 (annual) and 35 μg/m^3 (24-h) (U.S. EPA, 2013a). To comply with the standard, federal and state environmental protection agencies have planned and implemented emission mitigation strategies (e.g., National Clean Diesel Campaign; Cross-State Air Pollution Rule, formerly Clean Air Interstate Rule) to reduce particle pollution levels and thus protect human health and the environment (U.S. EPA, 2011a, 2011b).

The effectiveness of these policies can be evaluated by examining ambient pollutant concentration trends that are observed at a large number of ground compliance monitoring sites over time. However, the sampling frequency of these sites is usually every

three or six days in the U.S., and PM$_{2.5}$ monitoring networks are typically sparsely distributed and there are many geographical areas without monitoring sites. This may cause less reliable environmental assessments, leading to the necessity of spatially and temporally resolved methods for comprehensively evaluating the regulatory efforts. Satellite remote sensing is increasingly used to provide PM$_{2.5}$ information to complement ground PM$_{2.5}$ monitoring networks. The satellite data include aerosol optical depth (AOD), which provides information about the amount of aerosol in the atmosphere, and are available for different geographical areas without spatial limitations. Recently, we introduced models that used AOD data to predict daily surface-level PM$_{2.5}$ concentrations with reasonably high accuracy (Lee et al., 2011a, 2012), as discussed below.

The objective of our study was to estimate the PM$_{2.5}$ concentration trends (with the assumption of an identical percent change in concentrations per year) using daily satellite-based PM$_{2.5}$ predictions in the New England region, U.S. during the period 2000–2008. We first investigated the location-specific PM$_{2.5}$ concentration trends that varied spatially using satellite AOD (10×10 km resolution) and statistical models. The spatially and temporally resolved satellite-based PM$_{2.5}$ concentrations led us to assess location-specific (i.e., grid-specific) PM$_{2.5}$ trends throughout the study region. In combination with the seasonal variation of PM$_{2.5}$ concentration changes, this enabled us to evaluate the relative contributions of primary and secondary particles to the PM$_{2.5}$ mass trends and thus assess the effectiveness of PM$_{2.5}$ emission reduction policies. We further examined the trends of ground PM$_{2.5}$ species concentrations observed in the Boston area and compared them with source emission trends, while analyzing the relative impacts of primary and secondary pollutants on the observed PM$_{2.5}$ trends.

2. Methods

2.1. Satellite-based fine particulate matter concentrations

The PM$_{2.5}$ mass trend estimates were based on the PM$_{2.5}$ concentration predictions using satellite AOD data, previously developed by Lee et al. (2011a, 2012) and updated in this study. To develop the prediction models, we obtained filter-based PM$_{2.5}$ mass concentrations from 69 EPA monitoring sites and Moderate Resolution Imaging Spectroradiometer (MODIS) AOD values from the National Aeronautics and Space Administration (NASA) in Massachusetts, Connecticut, Rhode Island, Southern Maine, New Hampshire, and Vermont for the period 2000–2008. AOD values were provided by the MODIS due to its relatively fine spatial (10 km) and temporal (1–2 days) resolution compared to other available satellite sensors. The MODIS AOD data were calibrated using ground PM$_{2.5}$ measurements on a daily basis using a mixed effects model to predict PM$_{2.5}$ in the study region (Lee et al., 2011a). This MODIS daily calibration model generated day-specific PM$_{2.5}$-AOD relationships, as a combination of a fixed effect representing an average relationship for all days and a random effect explaining the daily variability of the relationship for each day. The model significantly improved the PM$_{2.5}$ predictive power in the study domain, which rendered AOD a robust predictor of PM$_{2.5}$. For days when AOD data were not available due to cloud, snow/ice cover, and retrieval errors (i.e., non-retrieval days), the spatial clustering method was shown to be useful to estimate the missing PM$_{2.5}$ concentrations (Lee et al., 2012). This modeling approach enabled all daily location-specific PM$_{2.5}$ concentrations to be estimated with reasonably high predictability. This study could contribute to acute and chronic health effect studies while providing spatially and temporally resolved PM$_{2.5}$ exposure estimates and thus reducing exposure errors. Taking advantage of the clustering method used in Lee et al. (2012), we performed the cluster analysis using the observed spatial variability of the PM$_{2.5}$ measurements over the study region in the current study. This cluster analysis identified groups (i.e., clusters) of days exhibiting similar spatial patterns of PM$_{2.5}$ concentrations, and a prediction model was developed for each cluster. In each cluster, we assumed that the relationship between average of PM$_{2.5}$ concentrations predicted from AOD data and average of regional PM$_{2.5}$ concentrations was constant and then calculated the ratio between the concentrations in each grid cell. This produced both cluster- and grid-specific ratios, and thus enabled us to predict all missing PM$_{2.5}$ concentrations. The regionally averaged PM$_{2.5}$ concentrations (i.e., average of all available PM$_{2.5}$ measurements on a given day) were available for all days. Using these two modeling approaches, daily ground PM$_{2.5}$ concentrations in each of the 579 grid cells (10×10 km^2) were estimated both for days with and without AOD data for a total of 3287 days.

2.2. Ground fine particulate matter species measurements

Ambient PM$_{2.5}$ samples were collected at the Harvard-EPA Clean Air Research Center monitoring site (42.34 °N, 71.10 °W) in Boston, MA from 2000 to 2008. This monitoring site has played a role in providing regionally representative data and thus PM$_{2.5}$ exposure estimates in epidemiological studies performed in the New England region, U.S. for more than a decade. At the monitoring site, daily 24-h integrated PM$_{2.5}$ samples were collected using the Harvard Impactor (Koutrakis et al., 1993). These samples were analyzed gravimetrically to determine daily PM$_{2.5}$ mass. Sulfate (SO$_4{}^{2-}$) concentrations were measured using ion chromatography before February 2, 2004. Since then, semi-continuous hourly measurements of SO$_4{}^{2-}$ using a sulfate particulate analyzer (Thermo Electron Corporation, model 5020, Franklin, MA) were employed to calculate 24-h averages. These two different methods for SO$_4{}^{2-}$ concentrations (i.e., ion chromatography and sulfate particulate analyzer) produced fairly equivalent results, as shown by Kang et al. (2010). SO$_4{}^{2-}$ concentrations were not available for a number of days in 2004, 2005, and 2006. Thus, we estimated missing data from sulfur concentrations by X-ray fluorescence analysis using a simple linear regression (correlation $r = 0.98$). Hourly ambient black carbon (a surrogate of elemental carbon) and particle number concentrations, measured with an Aethalometer (Magee Scientific Corporation, model AE-16, Berkeley, CA) and a Condensation Particle Counter (TSI Incorporated, model 3022 A, Shoreview, MN), respectively, were used to determine 24-h average black carbon and particle number concentrations. The same samplers and analytical methods for black carbon and particle number concentrations were constantly used for the entire study period. The black carbon concentrations measured by an Aethalometer may have bias caused by filter loading artifact (Arnott et al., 2005; Virkkula et al., 2007; Weingartner et al., 2003). However, in this study, we used the uncorrected black carbon concentrations because these values have been widely applied for health effect studies as exposure estimates in the study region. The total number of concentration is dominated by ambient ultrafine particles (< 0.1 μm) due to the higher number of distribution in the nucleation- (size range less than 0.01 μm) and the Aitken-modes (size range between 0.01 and 0.1 μm). More details about Harvard-EPA Clean Air Research Center measurements are described in Kang et al. (2010). It is noted that the sampling frequency at the monitoring site was every day, which provided more frequent species measurements and thus potentially more reliable trend estimates, compared to Chemical Speciation Network (CSN) monitoring sites generally with the sampling schedule of every three days.

We also obtained ambient PM$_{2.5}$ mass, SO$_4{}^{2-}$, nitrate (NO$_3^-$), organic carbon, and elemental carbon concentrations measured at a Chemical Speciation Network site (42.33°N, 71.08°W) in the Boston area for the same period (2000–2008). We used this Chemical Speciation Network monitoring site primarily to complement unavailable or very limited species concentration information (NO$_3^-$, organic carbon, and elemental carbon) at the Harvard-EPA Clean Air Research Center monitoring site. This monitoring site is located approximately 1.8 km away from the Harvard-EPA Clean Air Research Center monitoring site. The concentrations were determined by analyzing 24-h integrated PM$_{2.5}$ samples every three days. It is noted that this site used an identical carbon sampler for the period 2000–2008 (U.S. EPA, 2013b).

2.3. Data analysis

An autoregressive model was used to examine the trends of satellite- (PM$_{2.5}$ mass) and ground-based (PM$_{2.5}$, SO$_4{}^{2-}$, black carbon, and particle number) concentrations due to potential autocorrelations of time-series data. The autoregressive model produces more reliable error estimates for independent variables compared to a linear regression model without autoregressive errors. For the model, we first employed a stepwise autoregression method to select the final order of the autoregressive error model. This method sequentially tested autoregressive error models from high-order ones, resulting in all significant error lags left in the model ($p < 0.05$). Considering the residence time of PM$_{2.5}$ (days to weeks), PM$_{2.5}$ mass and species concentrations on lag 0 were much less likely to be correlated with those on lag day larger than 7 (one week). Due to potentially longer residence time, we decided to have an extra margin and thus ran the model with a starting lag of 25. The stepwise autoregressive model showed estimates of autocorrelations from lag 0 (correlation=1) to lag 25 with the corresponding p-values. This result demonstrated that autocorrelations generally became much smaller after the lag day of 3, indicating that the lag day of 3 was reasonable to estimate all the trend parameters in this analysis.

Because the concentration values were log-normally distributed we log-transformed them for the model calculations. Also, this transformation was based on the assumption that the percent change per year in the concentrations was constant throughout the study period. Despite the seasonal variations in ambient PM$_{2.5}$ mass and species concentrations, the assumption of constant annual percent changes is reasonable because the seasonal nature was evenly included in each year. To account for the annual trends, we considered the year as a continuous variable and used the year of 2000 as the baseline year. Daily satellite-predicted PM$_{2.5}$ mass concentrations in each of 10×10 km^2 grid cells allowed us to investigate grid-specific PM$_{2.5}$ mass trends. At the Harvard-EPA Clean Air Research Center monitoring site, there were more missing sampling days of the speciation compared to PM$_{2.5}$ mass. Thus, to compare trends for PM$_{2.5}$ mass and species concentrations, we selected only those days (a total of 2590 days) with valid

measurements of $PM_{2.5}$ mass, SO_4^{2-}, black carbon, and particle number. The concentrations generally showed monthly and day of week patterns, but the missing days were not equally distributed in each month and day of week. Since the distribution of the missing data could bias the yearly average concentrations and their subsequent trends, we added month (from January to December) and day of week (from Monday to Sunday) into the autoregressive models as categorical variables. Although we did not have missing satellite $PM_{2.5}$ predictions, we also added those variables into the satellite trend models to account for the periodic effects of month and day of week in each year, which was likely to estimate more accurate yearly concentration trends. The following equation of autoregressive models was used for the $PM_{2.5}$ trend analysis (the same type of equation was also used for all the species):

$$ln(PM_{2.5})_{i,j} = \beta_0 + \beta_1(Year)_j + \beta_2(Month)_j + \beta_3(Day\ of\ Week)_j + \varepsilon_{i,j} \qquad (1)$$

$$\varepsilon_{i,j} = \varphi_1 \varepsilon_{i,j-1} + \varphi_2 \varepsilon_{i,j-2} + \varphi_3 \varepsilon_{i,j-3} + \delta_{i,j}$$

where $(PM_{2.5})_{i,j}$ is the $PM_{2.5}$ concentration at a spatial location i on day j; $(Year)_j$, $(Month)_j$, and $(Day\ of\ Week)_j$ are the year, month, and day of week for day j, respectively; β_0 is an intercept of the autoregressive model; β_1 is the coefficient of the continuous $Year$ variable; β_2 is the coefficient of the categorical $Month_i$ (January–December) variable; β_3 is the coefficient of the categorical $Day\ of\ Week_j$ (Monday–Sunday) variable; $\varepsilon_{i,j}$, $\varepsilon_{i,j-1}$, $\varepsilon_{i,j-2}$, and $\varepsilon_{i,j-3}$ are the error terms at a location i for day j, $j-1, j-2$, and $j-3$, respectively; $\delta_{i,j}$ is the random error at a location i for day j. The slope (coefficient) of the year variable (β_1) can be used to estimate annual percent change (%) in the concentrations by calculating $[exp(\beta_1)-1] \times 100$. The seasonal concentration trends were also examined. The linear assumption between log-transformed concentrations and year was assessed by residual plots (i.e., residuals versus year), and the plots did not show clear curvature.

The absolute changes in concentrations ($\mu g/m^3$ or $counts/cm^3$) during the study period 2000–2008 were calculated as follows:

$$Absolute\ changes\ in\ concentrations =$$
$$model-estimated\ average\ PM_{2.5}\ concentration\ in\ 2000 \times [exp(\beta_1 \times 8)-1] \qquad (2)$$

The absolute concentration change was determined relative to the baseline concentration level in 2000. We did not consider meteorological variables in this study because meteorological data in each grid cell were not available for satellite-based $PM_{2.5}$ concentration trends. To be consistent, we did not control for the variables for ground $PM_{2.5}$ species trends as well.

2.4. Emission data

We compared the trends of ambient $PM_{2.5}$ species concentrations (SO_4^{2-}, NO_3^-, organic carbon, and black carbon/elemental carbon) measured in the Boston area

(i.e., Harvard-EPA Clean Air Research Center and Chemical Speciation Network sites) to those of their corresponding national and/or regional emissions [sulfur dioxide (SO_2), nitrogen oxide (NO_x), volatile organic compounds (VOCs), and highway $PM_{2.5}$] obtained from the National Emissions Inventory (U.S. EPA, 2011c, 2011d) and Clean Air Markets Division (Acid Rain Program) (U.S. EPA, 2013c). Finer spatial and temporal resolution of emission data for SO_2 and NO_x were provided by the Acid Rain Program, which requires regulated facilities to continuously monitor emissions. It is worth noting that the uncertainties of emission inventories vary by source type and need to be better quantitatively characterized, although the data have been substantially improved and are valuable for air quality management (NARSTO, 2005).

During the period 2000–2008, national emission data were available on a yearly basis (i.e., nine values for each emission), and state emission data were provided annually (SO_2 and NO_x) and for the years of 2002, 2005, and 2008 (highway $PM_{2.5}$). This prevented us from using the Eq. (1), and thus we estimated averages of 2000–2002 and 2006–2008 and subsequently the changes between the two periods for the national emission data. The statewide data including the states of Massachusetts, Connecticut, and Rhode Island were used to estimate averages of 2000–2002 and 2006–2008 for SO_2 and NO_x and to compare traffic $PM_{2.5}$ emissions for three individual years (2002, 2005, and 2008). All the associated concentration changes were investigated accordingly. It is noted that the chemical reactions of precursor VOCs to form secondary organic aerosols are complex and not fully understood (Kanakidou et al., 2005) and thus the comparison between them needs to be interpreted with caution. Also, there was a methodological change for estimating VOC emissions between 1999 and 2002, creating an artificial increase in national VOC emissions from 2001 to 2002 (Blanchard et al., 2013). Consequently, for the VOC emissions, we compared both the averages of 2000–2002 and 2002 to those of 2006–2008.

3. Results

3.1. Satellite-based fine particulate matter data

The model performed reasonably well with the high R^2 and a good agreement between the measured and predicted $PM_{2.5}$ concentrations [model $R^2 = 0.89$, slope $= 1.02$ (SE $= 0.004$), and intercept $= -0.09$ (SE $= 0.05$) for retrieval days; cross-validation $R^2 = 0.86$, slope $= 1.00$ (SE $= 0.005$), and intercept $= 0.10$ (SE $= 0.06$) for retrieval days; $R^2 = 0.79$, slope $= 1.02$ (SE $= 0.003$), and intercept $= 0.02$ (SE $= 0.03$) for non-retrieval days]. The nine-year average predicted $PM_{2.5}$ concentrations varied from 10.14 to 11.90 $\mu g/m^3$ in the 579 selected grid cells during the period 2000–2008 (Fig. 1A). The spatial variability in the
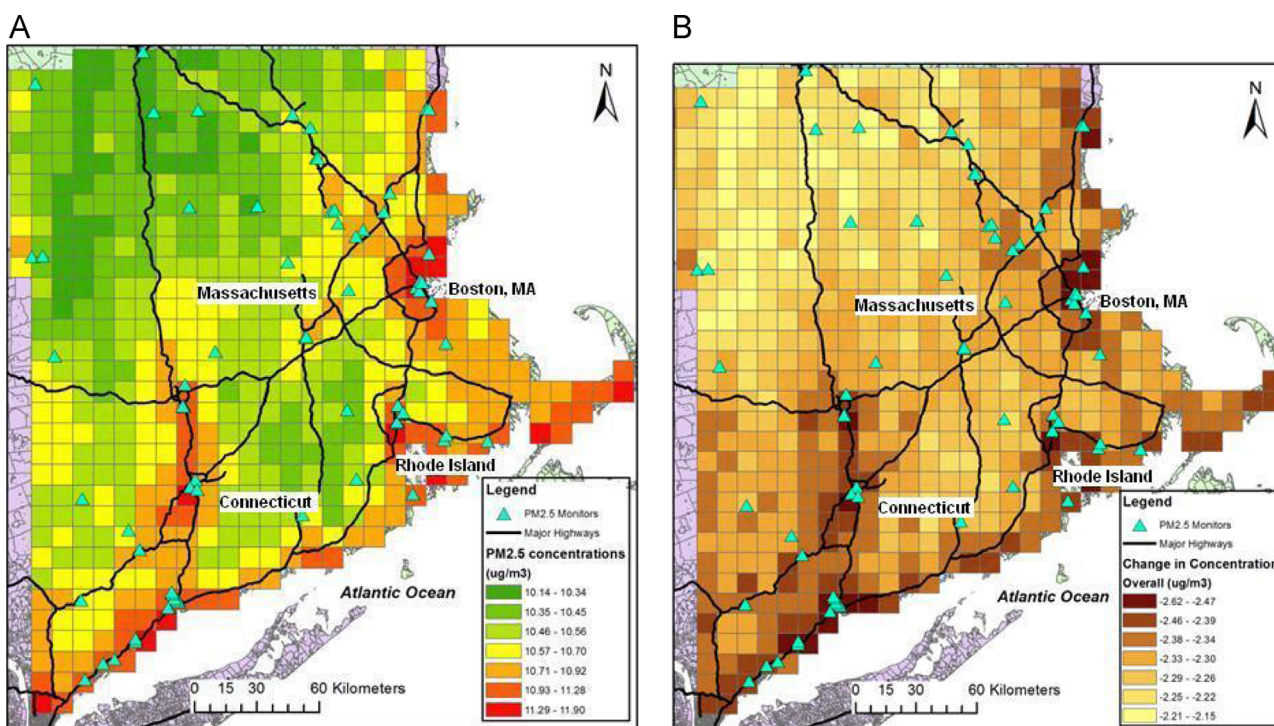
Fig. 1. Spatial variability in: (A) 2000–2008 nine-year average $PM_{2.5}$ concentrations and (B) $PM_{2.5}$ concentration decreases between 2000 and 2008 (Unit: $\mu g/m^3$). The $PM_{2.5}$ concentration decreases in each grid cell were statistically significant at the significance level of 0.05.

nine-year average PM$_{2.5}$ concentrations was relatively small. A good agreement between the measured and predicted PM$_{2.5}$ concentrations supports that the estimates were reasonable. Note that the grid-specific average values were based on daily (not every three or six days) PM$_{2.5}$ estimates for the 9 years and the spatial variability of daily concentrations was larger than that of 9-year average ones. The spatial pattern of PM$_{2.5}$, as shown in Fig. 1A, indicated large population and traffic areas and high point emission sources in the coastal cities (U.S. EPA, 2011d). The average concentrations across the New England region also varied by season, with the highest in the summer [12.82 (SD=7.69) μg/m^3], followed by winter [11.59 (SD=6.30) μg/m^3], fall [9.14 (SD=5.19) μg/m^3], and spring [8.87 (SD=4.61) μg/m^3].

Between 2000 and 2008, PM$_{2.5}$ mass concentrations decreased in all of the grid cells with concentration changes varying by location and season. As shown by Fig. 1B, grid-specific decreases in PM$_{2.5}$ mass concentrations ranged from 2.15 to 2.62 μg/m^3 and were more pronounced in urban areas compared to rural ones. The correlation between the average grid-specific absolute (μg/m^3) and relative (%) decreases in PM$_{2.5}$ concentrations was high (Pearson $r=0.67$), indicating a similar spatial variability in PM$_{2.5}$ concentration changes. The difference in PM$_{2.5}$ concentration changes between urban and rural areas was larger in winter compared to the one in summer. Fig. 2 depicts the seasonal decreases in satellite-derived PM$_{2.5}$ concentrations during the period 2000–2008. The decrease in PM$_{2.5}$ mass concentrations for winter ranged from 2.57 to 3.13 μg/m^3. In contrast, the decrease for summer varied from 1.10 to 1.42 μg/m^3, but significant annual PM$_{2.5}$ changes were not observed in any of the grid cells during this season [$p > 0.05$ for β_1 in Eq. (1)]. The decreases in PM$_{2.5}$ mass concentrations in the spring and fall were 2.31–2.91 μg/m^3 and 1.79–2.2 μg/m^3, respectively. All PM$_{2.5}$ changes in each grid cell were statistically significant ($p < 0.05$) during the winter, spring, and fall.

The New England region is mostly impacted by transported pollution (e.g., coal-fired power plants in the Midwest and traffic pollution from large metropolitan areas including New York City along the East coast) (Engel-Cox and Weber, 2007). Because of this high regional PM$_{2.5}$ background, the difference in concentrations between urban and rural areas is small, as shown in Fig. 1A. Thus,

the difference in the PM$_{2.5}$ trends between the two areas also tends to be relatively small (Fig. 1B).

During the winter, primary particles represent a larger fraction of PM$_{2.5}$ mass as compared to summer. This is because the rate of secondary particle formation is slower during this season. In addition, concentrations of secondary organic carbon precursor emitted from biogenic sources are considerably lower during the winter. Therefore, this difference between the winter and summer PM$_{2.5}$ mass trends (Fig. 2) suggests that primary particle concentrations decreased more relative to the secondary particle ones. This is also evidenced by the larger decrease in concentrations (μg/m^3) in urban areas and along the highways (Fig. 1B) which are relatively more impacted by primary emissions from local sources such as motor vehicles and possibly residential heating.

3.2. Fine particulate matter species measurements

The average PM$_{2.5}$ mass concentration measured at the Harvard-EPA Clean Air Research Center monitoring site was 10.23 (SD=6.53) μg/m^3 between 2000 and 2008. Also, the average SO$_4^{2-}$, black carbon, and particle number concentrations for the same period were 3.02 (SD=2.51) μg/m^3, 0.71 (SD=0.40) μg/m^3, and 22,254 (SD=12,501) counts/cm^3, respectively. The PM$_{2.5}$ mass, SO$_4^{2-}$, black carbon, and particle number concentrations varied by season (Table 1).

The overall and seasonal absolute and relative (percent) concentration changes in PM$_{2.5}$ mass, SO$_4^{2-}$, black carbon, and particle number are presented in Table 1. From 2000 to 2008, the PM$_{2.5}$ mass concentrations decreased by 2.29 μg/m^3 at an annual rate of 3.2% ($p < 0.0001$). This is fairly comparable to average 17% decrease of PM$_{2.5}$ mass concentrations in the U.S. between 2001 and 2008, as reported by U.S. EPA (U.S. EPA, 2010). For the same period, SO$_4^{2-}$, black carbon, and particle number concentrations were reduced by 0.46 μg/m^3 (2.4% year^{-1}, $p=0.0010$), 0.23 μg/m^3 (4.5% year^{-1}, $p < 0.0001$), and 18,025 counts/cm^3 (10.3% year^{-1}, $p < 0.0001$), respectively (Fig. 3). The concentration trends displayed a seasonal pattern with generally larger decreases in winter. Most of the pollutants exhibited more pronounced decreases during the winter: PM$_{2.5}$ mass (3.39 μg/m^3, 4.6% year^{-1}, $p < 0.0001$), black carbon (0.27 μg/m^3, 6.0% year^{-1}, $p < 0.0001$), and particle number (30,117 counts/cm^3, 11.6% year^{-1}, $p < 0.0001$). The larger decrease in elemental carbon concentrations during the winter compared to that during the summer in the U.S. was also observed by Murphy et al. (2011). However, the decreasing trend of SO$_4^{2-}$ concentrations was stronger in spring (0.84 μg/m^3, 4.7% year^{-1}, $p=0.0010$) than in either winter (0.61 μg/m^3, 3.2% year^{-1}, $p=0.0035$) or fall (0.61 μg/m^3, 3.6% year^{-1}, $p=0.0094$). SO$_4^{2-}$ concentrations increased by 0.41 μg/m^3 (1.7% year^{-1}, $p=0.3304$) in summer. Hand et al. (2012) found the decreasing trends of SO$_4^{2-}$ concentrations at most of monitoring sites in the U.S. during the summer of 2000–2010, although the statistical significance of the trends varied by site. This may be partly due to additional study period (2009–2010) which tended to be strongly affected by economic recession and thus large decline in SO$_2$ emissions.

As shown above, black carbon and particle number concentrations decreased at a higher rate than SO$_4^{2-}$ concentrations. To quantitatively examine the impact of SO$_4^{2-}$ and black carbon decreases on the PM$_{2.5}$ mass trends, we added log-transformed SO$_4^{2-}$ or black carbon concentrations into the Eq. (1) as an independent variable in two separate autoregressive models. By controlling for SO$_4^{2-}$ or black carbon concentrations, we can estimate the trends of PM$_{2.5}$ mass when either SO$_4^{2-}$ or black carbon did not change. The trend differences between adjustment and non-adjustment represent the PM$_{2.5}$ mass trends related to SO$_4^{2-}$ or black carbon changes. Controlling for SO$_4^{2-}$ reduced the PM$_{2.5}$ mass decrease to 1.7% year^{-1} ($p < 0.0001$) compared to 3.2%
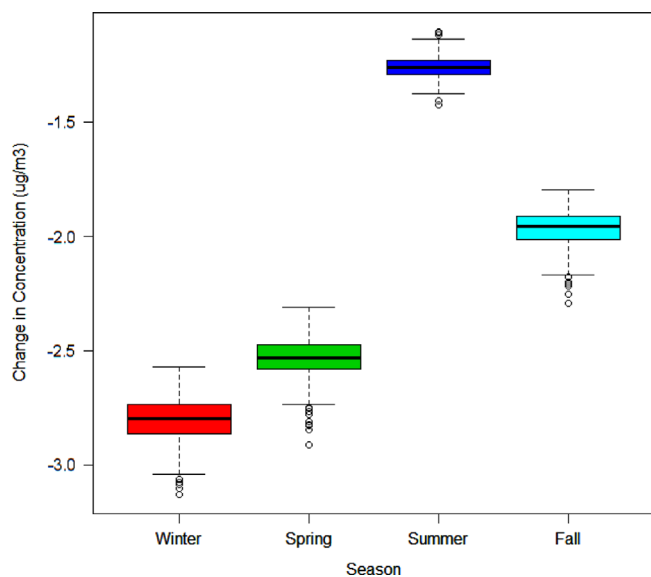
Fig. 2. Decreases in seasonal satellite-derived PM$_{2.5}$ concentrations between 2000 and 2008 (Unit: μg/m^3). Each boxplot represents changes in PM$_{2.5}$ concentrations estimated from each of 579 grid cells in the study region. The lower and upper limits of each box indicate 25th (lower quartile) and 75th (upper quartile) percentiles of the distribution, respectively. The whiskers cover from (lower quartile − 1.5 × interquartile range) to (upper quartile + 1.5 × interquartile range).

Table 1
Overall and seasonal changes in concentrations between 2000 and 2008 (Units: μg/m³ for change in PM₂.₅, SO₄²⁻, and black carbon; counts/cm³ for change in particle number; % for annual percent change). The concentration trends were based on ground measurements at the Harvard-EPA Clean Air Research Center monitoring site in Boston, MA.

	N	Mean[a]	SD	Change[b]	APC
Overall					
$PM_{2.5}$	2590	10.23	6.53	− 2.29	− 3.2
$SO_4{}^{2-}$	2590	3.02	2.51	− 0.46	− 2.4
Black carbon	2590	0.71	0.40	− 0.23	− 4.5
Particle number	2590	22,254	12,501	− 18,025	− 10.3
Winter					
$PM_{2.5}$	658	10.01	5.31	− 3.39	− 4.6
$SO_4{}^{2-}$	658	2.59	1.33	− 0.61	− 3.2
Black carbon	658	0.63	0.37	− 0.27	− 6.0
Particle number	658	32,001	13,279	− 30,117	− 11.6
Spring					
$PM_{2.5}$	662	8.57	4.77	− 2.48	− 4.0
$SO_4{}^{2-}$	662	2.59	1.76	− 0.84	− 4.7
Black carbon	662	0.56	0.32	− 0.23	− 5.4
Particle number	662	24,027	10,905	− 20,470	− 10.7
Summer					
$PM_{2.5}$	684	13.21	8.55	− 0.60	− 0.7[c]
$SO_4{}^{2-}$	684	4.18	3.60	0.41	1.7[c]
Black carbon	684	0.87	0.40	− 0.21	− 3.2
Particle number	684	13,843	6485	− 10,113	− 9.3
Fall					
$PM_{2.5}$	586	8.89	5.54	− 2.40	− 3.8
$SO_4{}^{2-}$	586	2.65	2.24	− 0.61	− 3.6
Black carbon	586	0.78	0.43	− 0.21	− 3.7
Particle number	586	19,126	10,355	− 14,132	− 9.4

[a] Mean is defined as arithmetic average.
[b] Change indicates absolute concentration change between 2000 and 2008.
[c] The annual percent change (APC) is not statistically significant at the significance level of 0.05.

year⁻¹ ($p < 0.0001$) without adjustment. Therefore, 1.5% of the annual PM₂.₅ decrease (i.e., 3.2%) was due to SO₄²⁻ and its associated components. However, after controlling for black carbon concentrations, no significant PM₂.₅ mass changes were found (+ 0.5% year⁻¹, $p = 0.3102$). Note that there was a moderate correlation ($r = 0.498$) between SO₄²⁻ and black carbon concentrations, which implies that the percent difference between the SO₄²⁻-adjusted and non-adjusted models (i.e., 1.5% year⁻¹) did not completely exclude the contribution of black carbon to the observed percent difference. This is also applicable to the percent difference between the black carbon-adjusted and non-adjusted models, which partly included the contribution of SO₄²⁻.

Table 2 shows the impact of primary emissions (U.S. EPA, 2011c, 2013c) on their associated ambient concentrations. We compared nationwide highway PM₂.₅ emissions to the concentrations of ambient black carbon (Harvard-EPA Clean Air Research Center) and elemental carbon (Chemical Speciation Network) measured in the Boston area. Although there might be other black carbon and elemental carbon emission sources, the observed day of week patterns for black carbon and elemental carbon (i.e., higher concentrations on the weekdays compared to those on the weekends) led us to focus on traffic PM₂.₅ emissions. When 3-year averages (i.e., 2000–2002 and 2006–2008) were compared, the highway PM₂.₅ emissions decreased by 26.8% from the earlier period (2000–2002) to the later one (2006–2008). At the same time, the ambient black carbon and elemental carbon concentrations decreased by 24.5 and 26.7%

between the two periods, respectively. The percent changes were quite comparable even with the potential bias due to other emission sources not considered. Between 2000–2002 and 2006–2008, the nationwide and state SO₂ emissions decreased by 25.7% and 57.5%, respectively. However, the ambient SO₄²⁻ concentrations measured at the Harvard-EPA Clean Air Research Center and Chemical Speciation Network Boston sites showed much lower reduction rates of 10.0% and 11.1%, respectively. The NOₓ emissions in the U.S. and New England decreased by 23.1% and 63.4% between 2000–2002 and 2006–2008, respectively, while the ambient NO₃⁻ concentrations measured at the Boston Chemical Speciation Network site decreased only by 7.3%. Further, the ambient organic carbon concentrations at the same Chemical Speciation Network site showed the decrease of 2.3%, whereas the national VOC emission decreased by 9.4% for the same period. When we compared 2002 VOC emissions to 2006–2008 emissions, the decrease in the national VOC emissions became larger (20.8%). Considering two major biogenic VOC components alone, the sum of terpene and isoprene was reduced by 12.3% nationwide and 11.7% in the New England region from 2002 to 2005 (U.S. EPA, 2011d). Organic carbon can be both primary and secondary, and the changes of primary and secondary organic carbon concentrations may differ due to their heterogeneous atmospheric processes. Therefore, the trends of primary and secondary organic carbon should be examined separately. For the analysis of secondary organic carbon concentration trend, we used elemental carbon as a tracer of primary organic carbon and estimated the secondary organic carbon concentration from the equations (Lim and Turpin, 2002): primary organic carbon = 1.8 × elemental carbon and thus secondary organic carbon = organic carbon–primary organic carbon, resulting in the 13.1% increase of secondary organic carbon between 2000–2002 and 2006–2008. The relationship between primary organic carbon and elemental carbon may vary by location (Blanchard et al., 2008). To account for the varying primary organic carbon to elemental carbon ratios by region, we performed a sensitivity analysis which showed that the increasing trends of secondary organic carbon concentrations ranged from 6.2% to 26.0% with the ratios of primary organic carbon to elemental carbon ranging from 1.2 to 2.5, respectively.

4. Discussion

In this study, we investigated the spatially varying PM₂.₅ mass concentration trends using PM₂.₅ prediction models developed by exploiting satellite AOD and spatial clustering. We also used ground speciation data to examine the trends of PM₂.₅ species concentrations in the study region. Together, our results suggest that the PM₂.₅ air quality improved considerably in the New England region during the period 2000–2008 and downward PM₂.₅ mass trends can be mostly attributed to primary emission decreases and their subsequent primary pollutant reductions.

Nationwide, PM₂.₅ emissions from highway vehicles decreased from 173 thousand tons (2000) to 107 thousand tons (2008) (U.S. EPA, 2011c). Specifically, in the states of Massachusetts, Connecticut, and Rhode Island, on-road vehicular PM₂.₅ emissions from overall and diesel vehicles decreased by 28.4% and 37.4% from 2002 to 2008, as reported by emission inventories (U.S. EPA, 2011d): 3544 and 2093 tons in 2002, 3069 and 1708 tons in 2005, and 2539 and 1310 tons in 2008, respectively. Note that we examined both national and New England region emissions given that the vehicular particles may be transported for long distance. Ban-Weiss et al. (2008) reported that the PM₂.₅ emission factors of light-duty vehicles and heavy-duty diesel trucks were reduced by 36 and 48% between 1997 and 2006, respectively. This can be attributed to retrofit technologies (e.g., diesel particulate filters and diesel oxidation catalysts), improved fuel efficiency, and
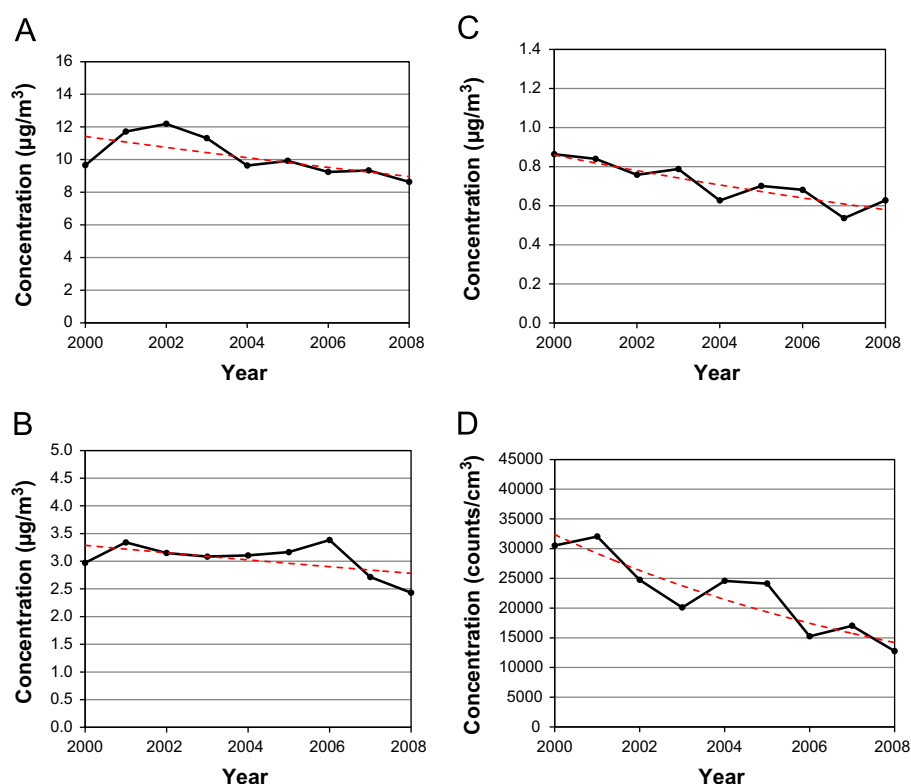
Fig. 3. Yearly average concentrations of (A) $PM_{2.5}$ mass, (B) SO_4^{2-}, (C) black carbon, and (D) particle number based on the identical sampling days (2590 days) for 2000–2008. The dashed line displays an exponential trend line of yearly average concentrations. Yearly average concentrations are defined as arithmetic averages of measured concentrations.

Table 2

Percent change (%) of primary emissions and their associated concentrations between 2000–2002 and 2006–2008 (Units: thousand tons for emission; $\mu g/m^3$ for concentration). For the comparison, on-road vehicular $PM_{2.5}$ emissions in the New England (NE) region decreased from 3.5 (2002) to 2.5 (2008) thousand tons (−28.4%). The % change in national VOC emissions from 2002 to 2006–2008 was -20.8%.

Emission[a]	Region	2000–2002	2006–2008	% Change
SO_2	U.S.	15,684	11,654	− 25.7
	NE	388	165	− 57.5
NO_x	U.S.	21,761	16,744	− 23.1
	NE	121	44	− 63.4
VOC	U.S.	18,596	16,853	− 9.4
Highway $PM_{2.5}$	U.S.	159	117	− 26.8
Concentration	**Site**			
SO_4^{2-}	Harvard	3.14	2.83	− 10.0
	CSN	3.13	2.78	− 11.1
NO_3^-	CSN	1.16	1.08	− 7.3
Organic Carbon	CSN	4.05	3.96	− 2.3
Black Carbon	Harvard	0.82	0.62	− 24.5
Elemental Carbon	CSN	0.87	0.64	− 26.7

[a] The national emission data were based on the version 1.5 of 2008 National Emissions Inventory.

cleaner fuels (U.S. EPA, 2011a). In addition, economic recession and high fuel price in 2008 (U.S. EIA, 2012) may further explain the larger decrease in diesel emissions from 2005 to 2008 (23.3%) compared to that from 2002 to 2005 (18.4%). Regarding home heating, the majority of U.S. residential fuel oil (i.e., No. 2 distillate oil) is consumed in the Northeast (approximately 84% in 2009) (U.S. EIA, 2011a). According to U.S. EIA (2011b), less No. 2 distillate oil for residential use was consumed in 2008 (1.7 billion gallons)

compared to in 2000 (2.3 billion gallons). The decreased consumption may be due to the replacement of oil boilers with natural gas boilers, better fuel efficiency, more efficient building insulation, and increasing oil market price (U.S. EIA, 2011c).

In Table 1 and Fig. 3, the ground speciation data showed that black carbon and particle number, indicating primary combustion pollution, decreased at higher rates than a secondary pollutant, SO_4^{2-}, between 2000 and 2008. The quantitative assessment provides strong evidence for the relative effects of black carbon and SO_4^{2-} on $PM_{2.5}$ mass concentration trends. The trend differences between black carbon or SO_4^{2-} adjusted and non-adjusted models indicate that both black carbon and SO_4^{2-} concentration changes contributed to the $PM_{2.5}$ mass trends, but the trends were more driven by primary pollutants including black carbon rather than secondary pollutants including SO_4^{2-}.

In the New England region, a primary pollutant black carbon is associated with both regional and local emissions from motor vehicles, residential heating (e.g., oil heating boilers) and cooking, and biomass burning. The ambient black carbon concentrations displayed a significantly higher concentration on weekdays ($p < 0.0001$) at the monitoring site. This indicates that black carbon concentrations were most likely to be derived from traffic sources, predominantly diesel emissions but not limited to local traffic. Murphy et al. (2008) showed that the day of week patterns of elemental carbon concentrations (i.e., minimum on Sunday) were pronounced even in remote and rural areas, indicating that transported diesel pollution can influence much wider areas than previously recognized.

The particle number concentrations mostly reflect the number of ambient ultrafine particles ($< 0.1\ \mu m$), indicating primary combustion pollution levels, usually from vehicular combustion exhaust (e.g., diesel-powered vehicles) (Shi et al., 1999; Zhu et al., 2002). The significantly higher particle number concentrations

during weekdays ($p < 0.0001$) provide evidence that it is mostly related to local sources. Unlike black carbon, the transport of ultrafine particles may be very limited, because of their relatively short atmospheric residence time due to their rapid coagulation onto accumulation mode (Hinds, 1999). The largest decreases in particle number concentrations (30,117 counts/cm^3, 11.6% year^{-1}) were shown in winter possibly due to vehicular emission trends. It is possible that particle number concentrations increase with decreasing PM$_{2.5}$ mass which is mostly present in the accumulation mode as a result of the lower ultrafine particle coagulation rates. However, in this analysis, both PM$_{2.5}$ mass and particle number concentrations decreased during the period between 2000 and 2008. This may be because of the use of more efficient emission control systems for removing ultrafine particles from the diesel engine exhaust. It can be also attributed to decreased sulfur content in diesel fuel since particle number concentrations depended on diesel sulfur content as shown by Jones et al. (2012) and Wang et al. (2011).

The sulfate particles impacting the Northeastern cities are transported from other regions (Lall and Thurston, 2006; Lee et al., 2011b; U.S. EPA, 2003). SO$_4^{2-}$ concentrations measured at the monitoring site in Boston presented a strong seasonal pattern ($p < 0.0001$), which showed the highest concentration during the summer. However, the SO$_4^{2-}$ concentrations did not show a significant day of week variability. These seasonal and day of week patterns are characteristics of regional pollutants whose impact is relatively homogeneous throughout the study region.

The similar decreases of source emissions (i.e., highway PM$_{2.5}$) and their associated ambient primary particle concentrations (i.e., black carbon and elemental carbon), as shown by Table 2, implicate that ambient concentrations of primary pollutants are directly influenced by emission changes. However, the decreasing rates of ambient SO$_4^{2-}$ concentrations were lower than those of primary SO$_2$ emissions. This may be due to the fact that secondary sulfate levels depend not only on the primary SO$_2$ emissions, which were likely to be reduced by legal actions against power generating utilities including retrofitting or shutting down the units, economic impacts, and partly 2006 highway diesel sulfur standards and 2007 heavy-duty vehicular emission standards (U.S. EPA, 2012), but also on the availability of oxidants in the atmosphere which might not change between 2000 and 2008. The non-linear relationship between other gaseous precursor emissions and ambient concentrations also provides evidence that oxidation rates (i.e., gas-to-particle conversion rates) increased during the period 2000–2008. The secondary particle concentrations (i.e., NO$_3^-$ and secondary organic carbon) decreased at a lower rate compared to their associated primary emissions (i.e., NO$_x$ and VOC) or even increased. This may be attributable to more available gaseous reactive species (e.g., ozone, hydroxyl radicals, peroxy radicals, and hydrogen peroxide) which cause more active secondary particle formation (U.S. EPA, 2004). It is supported by an increasing ozone concentration trend in the Boston area for 2000–2008 (3.2% year^{-1}, $p < 0.0001$) because the trend of ozone concentrations can indicate that of other atmospheric oxidants (Reid et al., 2001). The ozone concentration trend was estimated by constructing the same autoregressive model (i.e., Eq. (1)) with daily averages of hourly ozone concentrations measured at the Chemical Speciation Network site in the Boston area. Earlier work showed the non-linear relationship between SO$_2$ emissions or concentrations and SO$_4^{2-}$ concentrations, as found in this study (Jones and Harrison, 2011; Lovblad et al., 2004).

This trend analysis has several limitations. We compared the Boston pollutant levels to both national and regional emissions including three states of Massachusetts, Connecticut, and Rhode Island. However, it is difficult to determine the geographical boundaries of the sources that are mostly responsible for the observed pollutant trends in Boston. Uncertainty related to

satellite AOD retrievals and ground measurements might also affect the trend estimates found in this study.

This study suggests that satellite remote sensing, in combination with ground measurements, can be successfully applied to assess air quality trends. No previous studies have evaluated the effectiveness of emission control policies in the context of the spatially varying PM$_{2.5}$ trends using satellite AOD (579 grid locations), which expanded the spatial coverage of ground monitoring networks (69 ground monitoring locations). Also, the use of daily PM$_{2.5}$ species measurements for 9 years makes the air quality assessment more reliable. Moreover, the observed relationships between source emissions and primary and secondary particle concentrations are of substantial regulatory importance. As satellite technologies develop more spatially and temporally resolved PM$_{2.5}$ mass data will be able to further enhance our understanding of the effectiveness of previously implemented policy programs.

References

Arnott, W.P., Hamasha, K., Moosmuller, H., Sheridan, P.J., Ogren, J.A., 2005. Towards aerosol light-absorption measurements with a 7-wavelength Aethalometer: evaluation with a photoacoustic instrument and 3-wavelength mephelometer. Aerosol. Sci. Technol. 39, 17–29.

Ban-Weiss, G.A., McLaughlin, J.P., Harley, R.A., Lunden, M.M., Kirchstetter, T.W., Kean, A.J., et al., 2008. Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles. Atmos. Environ. 42, 220–232.

Bell, M.L., Ebisu, K., Belanger, K., 2007. Ambient air pollution and low birth weight in Connecticut and Massachusetts. Environ. Health Perspect 115, 1118–1124.

Bell, M.L., Belanger, K., Ebisu, K., Gent, J.F., Lee, H.J., Koutrakis, P., et al., 2010. Prenatal exposure to fine particulate matter and birth weight variations by particulate constituents and sources. Epidemiology 21, 884–891.

Blanchard, C.L., Hidy, G.M., Tanenbaum, S., Edgerton, E., Hartsell, B., Jansen, J., 2008. Carbon in southeastern U.S. aerosol particles: empirical estimates of secondary organic aerosol formation. Atmos. Environ. 42, 6710–6720.

Blanchard, C.L., Hidy, G.M., Tanenbaum, S., Edgerton, E.S., Hartsell, B.E., 2013. The Southeastern Aerosol Research and Characterization (SEARCH) study: temporal trends in gas and PM concentrations and composition, 1999–2010. J. Air Waste Manag. Assoc. 63, 247–259.

Dockery, D.W., Pope, C.A., Xu, X.P., Spengler, J.D., Ware, J.H., Fay, M.E., et al., 1993. An association between air pollution and mortality in six U.S. cities. New Engl. J. Med. 329, 1753–1759.

Engel-Cox, J.A., Weber, S.A., 2007. Compilation and assessment of recent positive matrix factorization and UNMIX receptor model studies on fine particulate matter source apportionment for the eastern United States. J. Air Waste Manag. Assoc. 57, 1307–1316.

Gent, J.F., Triche, E.W., Holford, T.R., Belanger, K., Bracken, M.B., Beckett, W.S., et al., 2003. Association of low-level ozone and fine particles with respiratory symptoms in children with asthma. J. Am. Med. Assoc. 290, 1859–1867.

Gent, J.F., Koutrakis, P., Belanger, K., Triche, E., Holford, T.R., Bracken, M.B., et al., 2009. Symptoms and medication use in children with asthma and traffic-related sources of fine particle pollution. Environ. Health Perspect. 117, 1168–1174.

Hand, J.L., Schichtel, B.A., Malm, W.C., Pitchford, M.L., 2012. Particulate sulfate ion concentration and SO$_2$ emission trends in the United States from the early 1990s through 2010. Atmos. Chem. Phys. 12, 10353–10365, http://dx.doi.org/10.5194/acp-12-10353-2012.

Hinds, W.C., 1999. Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles. Wiley, New York.

Jones, A.M., Harrison, R.M., 2011. Temporal trends in sulphate concentrations at European sites and relationships to sulphur dioxide. Atmos. Environ. 45, 873–882.

Jones, A.M., Harrison, R.M., Barratt, B., Fuller, G., 2012. A large reduction in airborne particle number concentrations at the time of the introduction of "sulphur free" diesel and the London emission zone. Atmos. Environ. 50, 129–138.

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., et al., 2005. Organic aerosol and global climate modeling: a review. Atmos. Chem. Phys. 5, 1053–1123, http://dx.doi.org/10.5194/acp-5-1053-2005.

Kang, C.M., Koutrakis, P., Suh, H.H., 2010. Hourly measurements of fine particulate sulfate and carbon aerosols at the Harvard-U.S. Environmental Protection Agency supersite in Boston. J. Air Waste Manag. Assoc. 60, 1327–1334.

Koutrakis, P., Sioutas, C., Ferguson, S.T., Wolfson, J.M., Mulik, J.D., Burton, R.M., 1993. Development and evaluation of a glass honeycomb denuder filter pack system to collect atmospheric gases and particles. Environ. Sci. Technol. 27, 2497–2501.

Lall, R., Thurston, G.D., 2006. Identifying and quantifying transported vs. local sources of New York City $PM_{2.5}$ fine particulate matter air pollution. Atmos. Environ. 40, S333–S346.

Lee, H.J., Liu, Y., Coull, B.A., Schwartz, J., Koutrakis, P., 2011a. A novel calibration approach of MODIS AOD data to predict $PM_{2.5}$ concentrations. Atmos. Chem. Phys. 11, 7991–8002, http://dx.doi.org/10.5194/acp-11-7991-2011.

Lee, H.J., Gent, J.F., Leaderer, B.P., Koutrakis, P., 2011b. Spatial and temporal variability of fine particle composition and source types in five cities of Connecticut and Massachusetts. Sci. Total Environ. 409, 2133–2142.

Lee, H.J., Coull, B.A., Bell, M.L., Koutrakis, P., 2012. Use of satellite-based aerosol optical depth and spatial clustering to predict ambient $PM_{2.5}$ concentrations. Environ. Res. 118, 8–15.

Lim, H.J., Turpin, B.J., 2002. Origins of primary and secondary organic aerosol in Atlanta: results' of time-resolved measurements during the Atlanta supersite experiment. Environ. Sci. Technol. 36, 4489–4496.

Lovblad, G., Tarrason, L., Torseth, K., Dutchak, S., 2004. EMEP assessment part I. Eur. Perspect. (accessed 25.06.13.)⟨http://emep.int/publ/reports/2004/assessment/Part1_001-010_00a-Title.pdf⟩.

Murphy, D.M., Capps, S.L., Daniel, J.S., Frost, G.J., White, W.H., 2008. Weekly patterns of aerosol in the United States. Atmos. Chem. Phys. 8, 2729–2739, http://dx.doi.org/10.5194/acp-8-2729-2008.

Murphy, D.M., Chow, J.C., Leibensperger, E.M., Malm, W.C., Pitchford, M., Schichtel, B.A., Watson, J.G., White, W.H., 2011. Decreases in elemental carbon and fine particle mass in the United States. Atmos. Chem. Phys. 11, 4679–4686, http://dx.doi.org/10.5194/acp-11-4679-2011.

North American Research Strategy for Tropospheric Ozone (NARSTO). 2005. Emission Inventory Assessments. Available: ⟨http://www.narsto.org/emission_inventory_1⟩ (accessed 8.11.13).

Ramanathan, V., Crutzen, P.J., Kiehl, J.T., Rosenfeld, D., 2001. Aerosols, climate, and the hydrological cycle. Science 294, 2119–2124.

Reid, N., Misra, P.K., Bloxam, R., Yap, D., Rao, S.T., Civerolo, K., et al., 2001. Do we understand trends in atmospheric sulfur species? J. Air Waste Manag. Assoc. 51, 1561–1567.

Shi, J.P., Khan, A.A., Harrison, R.M., 1999. Measurements of ultrafine particle concentration and size distribution in the urban atmosphere. Sci. Total Environ. 235, 51–64.

U.S. Energy Information Administration (U.S. EIA). 2011a. Use of heating oil. Available: ⟨http://www.eia.gov/energyexplained/index.cfm?page=heating_oil_use⟩ (accessed 22.11.11.).

U.S. Energy Information Administration (U.S. EIA). 2011b. Residential Fuel Oil Consumption. Available: ⟨http://www.eia.gov/petroleum/data.cfm#consumption⟩ (accessed 21.11.11.).

U.S. Energy Information Administration (U.S. EIA). 2011c. Residential Heating Oil Price. Available: ⟨http://www.eia.gov/dnav/pet/pet_pri_wfr_dcus_nus_w.htm⟩ (accessed 12.12.11.).

U.S. Energy Information Administration (U.S. EIA). 2012. U.S. On-highway Diesel Fuel Prices. Available: ⟨http://www.eia.gov/petroleum/gasdiesel/⟩ (accessed 28.12.12.).

U.S. Environmental Protection Agency (U.S. EPA), 2003. Compilation of Existing Studies On Source Apportionment for $PM_{2.5}$: Office of Air Quality Planning and Standards. Available: ⟨http://www.epa.gov/airtrends/specialstudies/compsareports.pdf⟩ (accessed 12.12.11.).

U.S. Environmental Protection Agency (U.S. EPA), 2004. Air Quality Criteria For Particulate Matter. Available: ⟨http://cfpub2.epa.gov/ncea/cfm/recordisplay.cfm?deid=87903⟩ (accessed 22.11.11.).

U.S. Environmental Protection Agency (U.S. EPA). 2010. Our Nation's Air- Particle Pollution. Available: ⟨http://epa.gov/airtrends/2010/report/particlepollution.pdf⟩ (accessed 18.11.11.).

U.S. Environmental Protection Agency (U.S. EPA), 2011a. National Clean Diesel Campaign (NCDC). Available: ⟨http://www.epa.gov/cleandiesel/index.htm⟩ (accessed 18.11.11.).

U.S. Environmental Protection Agency (U.S. EPA). 2011b. Cross-State Air Pollution Rule. Available: ⟨http://www.epa.gov/airtransport/⟩ (accessed 18.11.11.).

U.S. Environmental Protection Agency (U.S. EPA). 2011c. National Highway $PM_{2.5}$, SO_2, NO_x, and VOC Emission Trends. Available: ⟨http://www.epa.gov/ttn/chief/trends/index.html⟩ (accessed 7.12.11.).

U.S. Environmental Protection Agency (U.S. EPA). 2011d. National Emissions Inventory- State. Available: ⟨http://www.epa.gov/ttn/chief/eiinformation.html⟩ (accessed 22.11.11).

U.S. Environmental Protection Agency (U.S. EPA). 2012. Diesel Fuel- Regulations and Standards. Available: ⟨http://www.epa.gov/otaq/fuels/dieselfuels/regulations.htm⟩ (accessed 28.12.12.).

U.S. Environmental Protection Agency (U.S. EPA). 2013a. Regulatory Actions: 2012 Annual $PM_{2.5}$ Standard. Available: ⟨http://www.epa.gov/air/particlepollution/actions.html#dec12⟩ (accessed 20.04.13.).

U.S. Environmental Protection Agency (U.S. EPA). 2013b. Chemical Speciation-URG3000N Carbon Implementation. Available: ⟨http://epa.gov/ttn/amtic/specurg3000.html⟩ (accessed 17.12.13.).

U.S. Environmental Protection Agency (U.S. EPA). 2013c. Air markets Program Data. Available: ⟨http://ampd.epa.gov/ampd⟩ (accessed 2.07.13.).

Virkkula, A., Makela, T., Hillamo, R., Yli-Tuomi, T., Hirsikko, A., Hameri, K., et al., 2007. A simple procedure for correcting loading effects of aethalometer data. J. Air Waste Manag. Assoc. 57, 1214–1222.

Wang, Y.G., Hopke, P.K., Chalupa, D.C., Utell, M.J., 2011. Long-term study of urban ultrafine particles and other pollutants. Atmos. Environ. 45, 7672–7680.

Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., Baltensperger, U., 2003. Absorption of light by soot particles: determination of the absorption coefficient by means of aethalometers. J. Aerosol. Sci. 34, 1445–1463.

World Health Organization (WHO). 2005. WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide And Sulfur Dioxide: Global update 2005. Available: ⟨http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf⟩ (accessed 15.11.13.).

Zhu, Y.F., Hinds, W.C., Kim, S., Sioutas, C., 2002. Concentration and size distribution of ultrafine particles near a major highway. J. Air Waste Manag. Assoc. 52, 1032–1042.